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Freddy Strømmen

Freddy Strømmen
Seksjonsleder

Line Reum

Line Reum

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NORWEGIAN PATENT APPLICATION NO.

ABC-Patent: NNP01383A

Title: Fiber optical sensor.

Applicant: OPTOPLAN AS
Bjørkhaugvn. 27
N-7002 TRONDHEIM
Norway

Inventor: Arne Berg
Vipevn. 10
N-7082 KATTEM
Norway

Agent: Rolf Chr. B. Larsen in the firm
ABC-Patent, Siviling. Rolf Chr. B. Larsen a.s

This patent application is related to a sensor system for the detection or measurement relating to a chemical environment.

Background art

It is well known that hydrogen gas can diffuse into optical fibres and generate additional transmission loss at certain wavelengths [1]. Due to its small size, the hydrogen gas molecule, H_2, which in many situations is present around an optical fiber, can diffuse into the central light-guiding core region of the optical fiber, causing increases in the optical loss of the fiber. Traditionally, this has been regarded as an undesired effect, as increased loss implies reduced information transmission capacity in fibre-optic based long-haul optical communication systems. Such loss could for example be due to hydrogen originating either from polymeric materials or from galvanic corrosion cells present in submerged cables [1]. Such problems have been dealt with by altering the fibre dopant composisitons, redesign of the fiber cables to avoid the possibility of hydrogen generation and employing steel tube protection around the optical fibres to block the diffusion of any hydrogen that might be present in a cable [1].

The invention

We have realized that the diffusion of hydrogen into optical fibres is not only an undesired effect, but can be used advantageously to detect or measure hydrogen directly and/or other gases and liquids indirectly by the use of the above described effect.

Hence, the major objective of the present invention is to provide a system for monitoring the chemical environment in surroundings where optical fibres can be placed and used as a sensor.

In particular it is an objective of the invention to provide an apparatus which can be used as a sensor for monitoring flexible risers in offshore environments.

According to the invention, these objectives are achieved by a system according to the independent claim 1. Further embodiments of the invention are given in the dependent claims.

The particular objective of monitoring flexible risers in offshore environments is achieved by using a sensor system according to the invention for monitoring the corrosion and/or the environmental conditions of the risers.

The invention will now be explained in detail, with reference to the enclosed drawings. In the drawings,

Fig. 1 illustrates schmatically a sensor system where reaction elements or catalyzers are exposed to a chemical environment.

Fig. 2 illustrates schematically a distributed sensor system with a read-out unit of the OTDR or Bragg type.

Fig. 3 illustates a cross-section of a riser with armour wires,

Fig. 4 illustrates a cross-section of two neighbouring armour wires with embedded optical fibre and reactant/catalyzer and,

Fig. 5 illustrates a cross-section of two neighbouring armour wires with a reactant/catalyzer directly exposed to the chemical environment.

Fig. 1 illustrates schematically a sensor system 1 for measurement in a surrounding chemical environment 2. The optical part of the system comprises a light source 6 launching light into an optical fibre 3. The optical fibre is arranged to allow a gas, e.g. hydrogen, derived from the chemical environment 2 to diffuse into at least a part of the optical fibre 3. The gas diffusing into the optical fibre

change the transmission characteristics (e.g. transmission loss) of the optical fibre 3.

The gas can be derived from the chemical environment 2 by generation in chemical processes (e.g. corrosion) normally initiated by the chemical environment itself. Additionally, the gas can be derived from the chemical environment by the placement of additional elements 16, e.g. reactants or catalyzers, that generate hydrogen gas directly when the materials to be detected (e.g. water) appears in the chemical environment 2. The additional elements may not generate the gas directly, but could also generate a gas indirectly by taking part in a chemical process resulting in the generation of the gas, e.g. hydrogen. Upon diffusing into the core of the optical fibre the gas, e.g. hydrogen, causes an additional optical loss in the fibre. This additional loss can be measured and the fibre thereby represents a sensing element for the detection of constituents of the chemical environment which initiates the formation of the gas causing this additional loss.

The sensor system 1 may comprise inlet means 8 to allow a part or sample of the chemical environment to enter the sensor system. In this case one or more reaction elements or catalyzers 16 are arranged on the inside of the the inlet means as with regard to the chemical environment in such a way that the reaction elements or catalyzers only react with the part or sample of the chemical environment that passes through the inlet means 8. The inlet means 8 may have a control function in order to allow parts or samples of the chemical environment 2 to enter the sensor system at given times, during given periods, at given temperatures of the chemical environment or other predetermined conditions. The inlet means 8 may also comprise selective membranes for allowing only specific constituents of the chemical environment to enter the sensor system. Having the reactive elements or catalyzers 16 inside inlet means may have the

advantage of making it easier to control or monitor the temperature and other conditions of the elements.

Figure 2 illustrates an example of the system in a distributed sensor configuration. Two reaction elements or catalyzers 16, which may be of similar or dissimilar types, are placed at different positions along the length of the optical fibre 3. The optical fibre extends some distance into the chemical environment 2 to be monitored. Alternatively, several reaction elements or catalyzers 16 are placed at practically the same position. A read-out unit 30 may comprise signal detection 4 and signal analysing means 5 adapted for OTDR-measurements (optical time domain reflectometry) in order to resolve measurement positions along the length of the optical fibre 3.

In an alternative the optical fibre may comprise Bragg gratings placed along the length of the optical fibre. In this case the read-out unit 30 comprises a Bragg-wavelength read-out section for the separation of the Bragg wavelength of each Bragg grating along the optical fiber. Bragg gratings are typically placed next to reaction elements or catalyzers 16.

An example of an application of the sensor principle is corrosion monitoring of flexible risers. Risers 10, as llustrated in Figure 3, are made of various layers of metal and polymer to achieve the required performance. The tensile armouring 11 is included to make the riser withstand tension is located in an annulus between the extruded polymer layers 20. In addition, a pressure armouring layer 21 is normally included in the riser. The armour wires 11 are dimensioned to withstand the generated forces and the fatigue stress due to riser bending during the riser lifetime. However, corrosion of the armouring wires 11 will have serious impact on the safety and lifetime of the riser 10. It is therefore important to detect any start of corrosion (hydrogen generation). Corrosion will start due to the ingress of water. Gases like carbon dioxide and hydrogen sulfide will

strongly influence on the corrosion process. It would be very important to detect the appearance of these gases.

A technique to integrate small metal tubes with fibres and/or fibre Bragg gratings along the tensile wires have been worked out. As illustrated in Figure 4, the tubes 13 are bonded or encapsulated into grooves 12 in the sidewalls of the wires 11. Suitable encapsulants may be epoxies, polyurethanes, silicones or any other commonly used encapsulant, adhesive or sealing material. The wires 11 are terminated in the riser endfitting, and the sensor tubes can be connected to an external cable with the read out unit in a control room at the other end of the cable (to measure transmission loss).

The corrosion sensing system can detect hydrogen generated from the corrosion process itself or reactants can be utilised. Reactants 16 can be embedded in the encapsulant 15 in the same manner as for bonding the fibre tube 13, , applied onto the armouring wires 11 themselves or as separate elements in the annulus. Separate elements can for instance be mounted in similar grooves opposite to the grooves with the fibre sensors, as illustrated in Figure 4. Reactants sensitive to water, carbon dioxide, hydrogen sulfide and/or other materials to be detected can be applied. As illustrated in Figure 5, the reactants 16 can be embedded in epoxy 15 in a groove 12 of the armour wire 11 in such a way that a polishing process exposes a surface of the reactant or catalyzer to the chemical environment 2.

The reactant 16 can also represent a galvanic protection of the wire 11 when the reactant material 16 represents a sacrificial anode with respect to the steel wire.

The additional loss caused by the gas diffusing into the optical fibre can be measured by monitoring the transmission loss. Optical signal detection means 4 and signal analysing and processing means 5 are adapted for determining changes in the optical properties of the optical fibre due to the additional loss caused by the in-diffusion of the said gas.

The signal analysis and processing means 5 is adapted to derive from the determined changes at least one characteristic value representing the chemical environment 2. By using an optical time domain reflectometer (OTDR) technique the location of the additional loss along the optical fibre can also be determined.

In fibre Bragg gratings (FBG) indiffusion of hydrogen causes a change in the effective refractive index and will thereby generate a small shift in the reflected Bragg wavelength. Such a shift will represent a change in the environmental conditions. The shift can be monitored and a fibre Bragg grating can be used as a sensing element for hydrogen detection.

The additional loss in an optical fibre or change of Bragg wavelength in a fibre Bragg grating depends on the hydrogen concentration in the core of the fibre where the light is guided and the core materials, e.g. glas dopants. The diffusion time for the hydrogen gas to penetrate into the fibre core depends on the fibre dimensions, coatings and temperature.

Other effects than hydrogen gas, like micro- and macro bends, can also generate transmission loss in an optical fibre. The sensitivity and measuring accuracy can be improved by using a reference monitoring technique. The hydrogen can be detected more specifically by monitoring the transmission loss at the absorption peak (1244 nm). By measuring the loss at another wavelength besides the absorption peak (e.g. 1300nm), this loss can be used as reference. The differential additional loss will then only be due to hydrogen and the monitoring accuracy can be improved considerably.

The reflected wavelength of a Bragg grating also depends on the temperature and strain in the fibre. Such effects can be compensated by putting two gratings close by where both are exposed to the same strain and temperature, but one is protected from hydrogen (e.g. by a carbon layer). The differential shift of the Bragg wavelength will then only be

due to hydrogen and the monitoring accuracy can be improved considerably.

An optical fibre can be placed directly in the area to be monitored, but because of the material (glas) and typical dimensions of optical fibres (diameter in the order of 0.1mm), it represents a fairly vulnerable sensing element. To increase the strength optical fibres are usually protected by some type of coating. For ordinary tele- and data communications, one or two layers of acrylate are frequently used (overall outer diameter 0.25mm). For applications at higher temperature, polyimide is often applied. Metal coated fibres can be used at even higher temperatures.

Even with polymer layers an optical fibre is not very rugged. However, optical fibres can be packaged inside small tubes of different materials (f. inst. steel) for protection. The tubes can be installed in the areas to be monitored and thereby represents a sensing element for environmental monitoring. Loss monitoring in a fibre will be a continuous sensor, while Bragg gratings will represent sensors at specific points.

The tube material and dimensions (outer diameter and wall thickness) will influence on the diffusivity of hydrogen gas into the fibre (or Bragg grating) and the overall sensitivity and time constant of the sensor system.

Based on the presented fibre optic sensing techniques and the possibility for hydrogen detection, various sensing configurations can be utilised. The most direct monitoring will be for processes that generates hydrogen themselves, like corrosion of metal. Corrosion is a reaction usually separating water into hydrogen and a metal oxide.

To make the sensing system more effective and/or more selective, an additional reactive element can be applied. As an example ordinary iron can be used in the sensor to detect water even though the construction is made of stainless steel.

To detect other substances, components that reacts efficient with these substances can be utilised. For example, carbondioxide (CO_2) and hydrogensulfide (H_2S) can be detected by measuring the hydrogen generated when these dissolves in water in the presence of suitable reactants. H_2S hydrolyzes (dissolves) in water and, depending on the pH, ionizes to establish an equilibrium with H^+, HS^- and $H_2S(aq)$. CO_2 dissolves in water and establishes an equilibrium with $H_2CO_3(aq)$, which further, depending on the pH, ionizes to form H^+, HCO_3^- and CO_3^{2-}. The solubility of zinc (Zn) and magnesium (Mg) is proportional to the H^+-concentration in the solution, subject to the condition that there are no passivating surface films. These metals will react and form H_2 which can be detected. This will yield the pH of the solution and a good indication of the rate of corrosion in anaerobic conditions.

Separate measurement of CO_2 and H_2S may be more difficult. A possible solution would be to use chemicals which react selectively with H_2S forming H_2 and sulfates. H_2S is a weakly oxidating material, but would be able to reduce e.g. Fe_3^+ to Fe^{2+} and MnO_2 to Mn^{2+}. This reaction forms sulphur and H^+, yielding an increase in pH in the surrounding environment which normally would be detectable using eg. a reaction with zinc to indicate H_2S.

There are of course a variety of other material combinations that can be used to generate hydrogen to utilise the sensing principle.

Based on presented techniques for fibre packaging, various sensing elements can be made. The sensitivity of the fibre itself can be optimised by using a fibre with e.g. germanium dopants in the core. To detect hydrogen most efficiently, only polymer coatings (with high diffusivity to hydrogen) should be applied onto the fibre. To increase sensitivity, a reactive element can be added to or on the outside of the fibre coating. The generation of hydrogen will then take place close to the fibre and the sensing system can then utilise the gas efficiently.

Fibre protection by an outer tube makes it possible to add the reactive element in the tube wall or at the outside. Various elements can easily be added in or at the surface of polymer tubes. Protective tubes made of materials with high diffusivity will not influence much on the response time either.

For protective metal tubes the metal itself can be the reactive element, or a layer of reactant can be deposited outside. Metal tubes represent a rugged protection, but is also a barrier to hydrogen diffusion that will effect sensitivity and response time. The tube material and wall thickness can be selected to optimise the sensing performance. A polymer or other suitable material outside the metal tube can include the reactant to assure that the hydrogen generation takes place close to the tube wall.

The reactant can also be applied as a part of a separate element in the area to be monitored to start the generation of hydrogen gas. The reactant can also be applied on all or some of the parts that represents the surroundings to be monitored.

For some applications the reactant can be a liquid or a part of a mixture (fluid or grease) that is enclosed in the area to be monitored.

The sensing principle is based on the detection of hydrogen gas. When the hydrogen is a result of oxidation of the reactant in the sensor system, this is a nonreciprocal process. The reactant will be consumed and can not be replaced without replacing the reactant element itself. If, however, a catalyzer is used, the catalyzer will normally not be consumed in reaction process.

In fibres with dopants in the core, some of the additional loss is permanent and the loss will not return to its initial value even though the hydrogen is removed from the fibre core (out diffusion).

These limitations might not represent severe problems in applications where the major objective is to detect whether a material has appeared (alarm function) or that a critical process has started (e.g. corrosion).

References

[1] "Reliability of optical fibers exposed to hydrogen: prediction of long-term loss increases", P. J. Lemaire, i *Optical Engineering,* June 1991, Vol. 30, no. 6.

P a t e n t k r a v

1. Sensor system for the detection or measurement relating to a chemical environment (2), comprising
an optical fibre (3),
an optical source (6) for launching light into the optical fibre (3),
the sensor system being adapted to let a gas, e.g. hydrogen derived from said chemical environment (2), diffuse into the optical fibre thereby altering the optical properties of the optical fibre,
optical signal detection (4) and signal analysing means (5) adapted for determining changes in the optical properties of the optical fibre (3) due to the in-diffusion of the said gas,
and the signal analysis means (5) is adapted to derive from the determined changes at least one characteristic value representing the chemical environment (2).

2. Sensor system according to claim 1,
comprising reaction elements or catalyzers (16) adapted to react with constituents of the chemical environment (2) creating said gas in the reaction.

3. Sensor according to claim 2,
wherein the reactive element(s) or catalyzer(s) (16) is/are added to or on the outside of the fibre coating of the optical fibre (3).

4. Sensor according to claim 2,
wherein the reactive element(s) or catalyzer(s) (16) is/are added to or on the outside of a tube element provided for protection and packaging of the optical fibre (3).

5. Sensor according to claim 2,
wherein the one or more reactive elements or catalyzers (16) comprises elements capable of undergoing a chemical reaction, such as a corrosion process, thereby generating said gas, e.g. hydrogen.

6. Sensor according to claim 5,
wherein the one or more reactive elements or catalyzers (16) comprises metals.

7. Sensor according to claim 6,
wherein the metal elements comprises iron, the iron generating hydrogen, and
the signal analysis means are adapted to derive from the determined changes a value representing the ingress of water and the start of a corosion process.

8. Sensor according to claim 6,
wherein the metal elements comprises zinc,
the zinc generating hydrogen, and
the signal analysis means are adapted to derive from the determined changes a pH-value representing the chemical environment.

9. Sensor system according to one of the preceding claims, wherein the in-diffusion of said gas causes an additional loss in the light transmitted in the optical fibre.

10. Sensor system according claim 9,
comprising optical transmission measurement means for obtaining a measure of the additional loss by measuring the transmission loss of the optical fibre.

11. Sensor system according to claim 9 or 10, comprising optical measurement means, for example an OTDR(Optical Time Domain Reflection)-apparatus for determining the magnitude and location of the additional losses along the fibre.

12. Sensor system according to claim 10 or 11, further comprising optical measurement means for measurement of at least two optical wavelengths, the first optical wavelength being within an absorption peak caused by the gas, e.g. at at 1244 nm for hydrogen, the second optical wavelength being outside the absorption peak caused by the gas, e.g. at about 1300 nm for hydrogen, comparison means for comparing the measurements at said at least two wavelengths in order to compensate for losses caused by other mechanisms than in-diffusion of the gas, e.g. bending of the fiber.

13. Sensor according to claim 1, wherein the optical fibre comprises one or more FBG(Fiber Bragg grating)-elements, the Bragg wavelength of the Bragg grating(s) depending on the in-diffusion of said gas, and the optical detection and signal analysing means comprises means for measuring the shift of the reflected Bragg wavelength of at least one of the FBG elements due to the in-diffusion of said gas.

14. Sensor according to claim 13, comprising means for compensating for wavelength changes caused by other mechanisms than in-diffusion of the gas, for example temperature changes, by measurement of at least two FBGs, preferably closely spaced, where at least one FBG is exposed to the gas and at least one other FBG is protected from the gas.

15. Sensor according to claim 14,
wherein a carbon layer is provided for protection.

16. Sensor according to any of the preceding claims,
wherein the change in the optical properties of the optical fibre is enhanced by suitable dopants in the fibre, e.g. germanium or phosphorous.

17. Sensor according to any of the preceding claims,
comprising a material with high diffusivity to the gas, e.g. polymers with high diffusivity to gas, in the fibre coating.

18. Sensor according to claim 6,
wherein the metal elements comprises magnesium, in order to enable the detection or measurement of carbon dioxide by detection or measurement of the hydrogen formed during a reaction process including the carbon dioxide and metal elements

19. Sensor according to claim 6,
wherein the metal elements comprises zinc, in order to enable the detection or measurement of hydrogen sulfide by detection of the hydrogen gas formed in a reaction process including the hydrogen sulfide and the metal elements.

20. Sensor according to any one of the preceding claims,
wherein inlet means (8) are arranged to allow a sample or part of the chemical environment (2) to enter the sensor system (1).

21. Sensor according to claim 2,
wherein the one or more reaction elements (16) contribute to the galvanic protection of the metal armouring (11).

22. Use of sensor system according to any one of the preceding claims as a sensor for monitoring the corrosion and/or the environmental conditions of flexible risers in offshore environments.

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S a m m e n d r a g

A sensor system for the detection or measurement relating to a chemical environment (2), comprising
an optical fibre (3),
an optical source (6) for launching light into the optical fibre (3),
the sensor system being adapted to let a gas, e.g. hydrogen derived from said chemical environment (2), diffuse into the optical fibre. The gas thereby alters the optical properties of the optical fibre. The system comprises optical signal detection (4) and signal analysing means (5) adapted for determining changes in the optical properties of the optical fibre (3) due to the in-diffusion of the said gas. The signal analysis means (5) is adapted to derive from the determined changes at least one characteristic value representing the chemical environment (2).

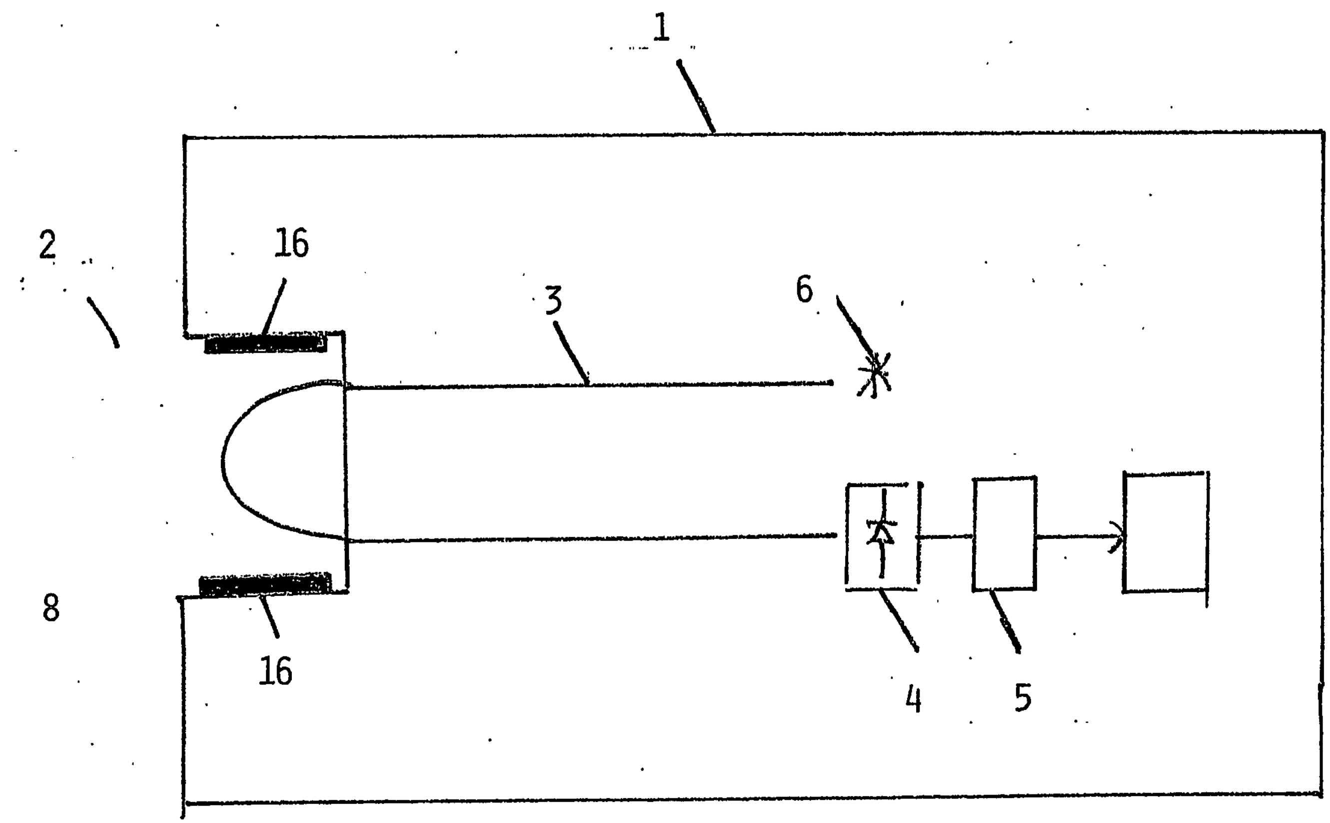

FIG. 1

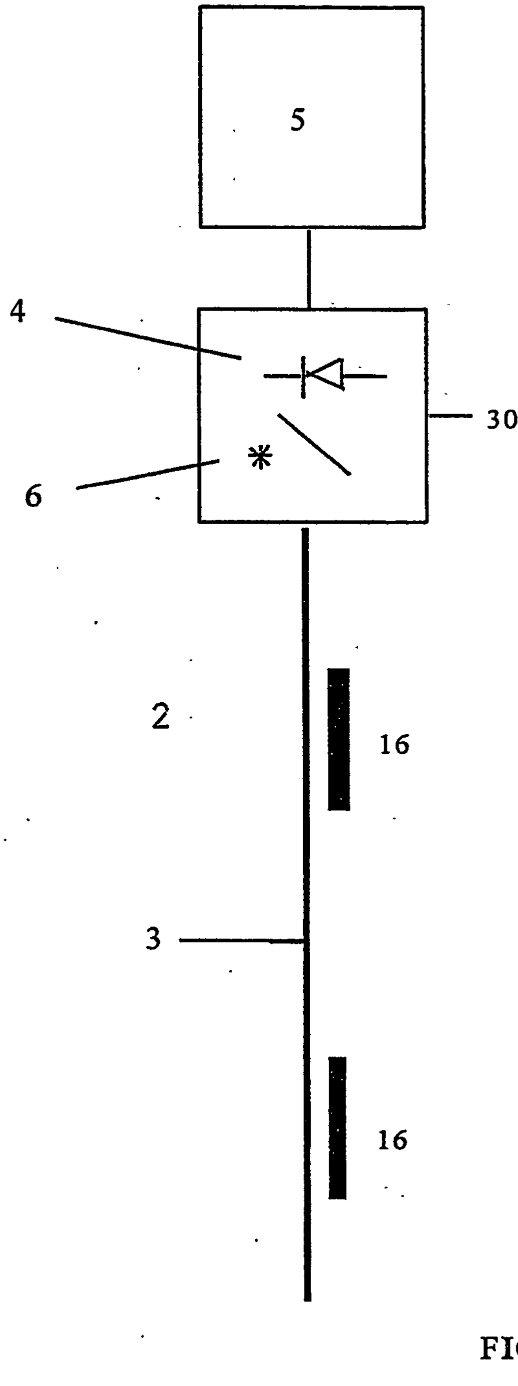

FIG. 2

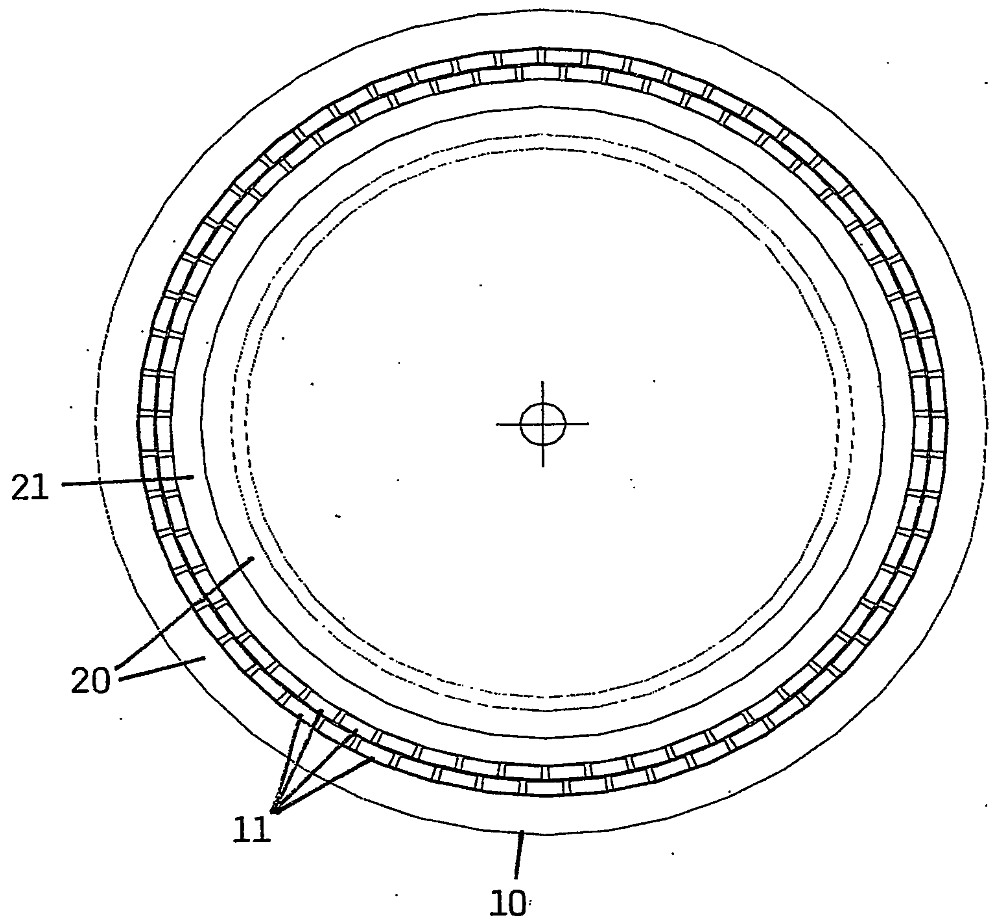

FIG. 3

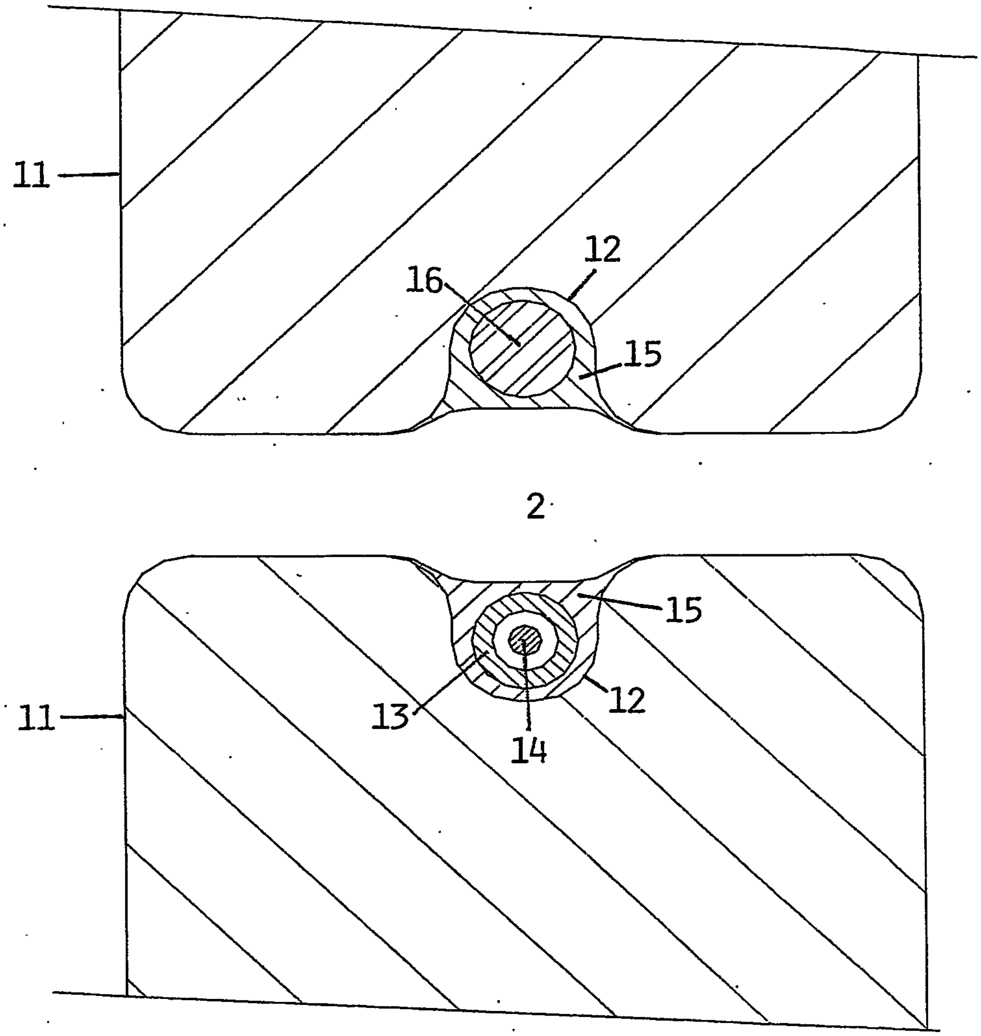

FIG. 4

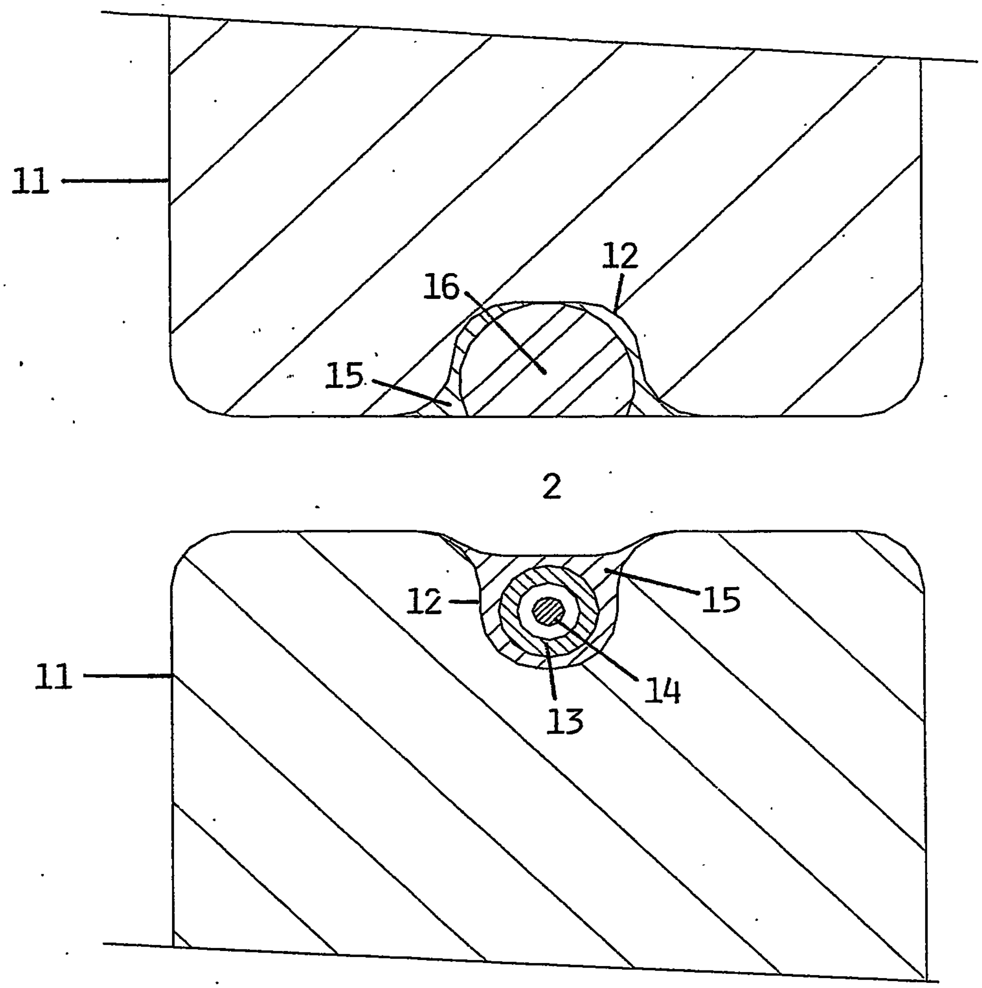

FIG. 5